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Transformation Pathways of Hexachlorocyclopentadiene in the Aquatic Environment

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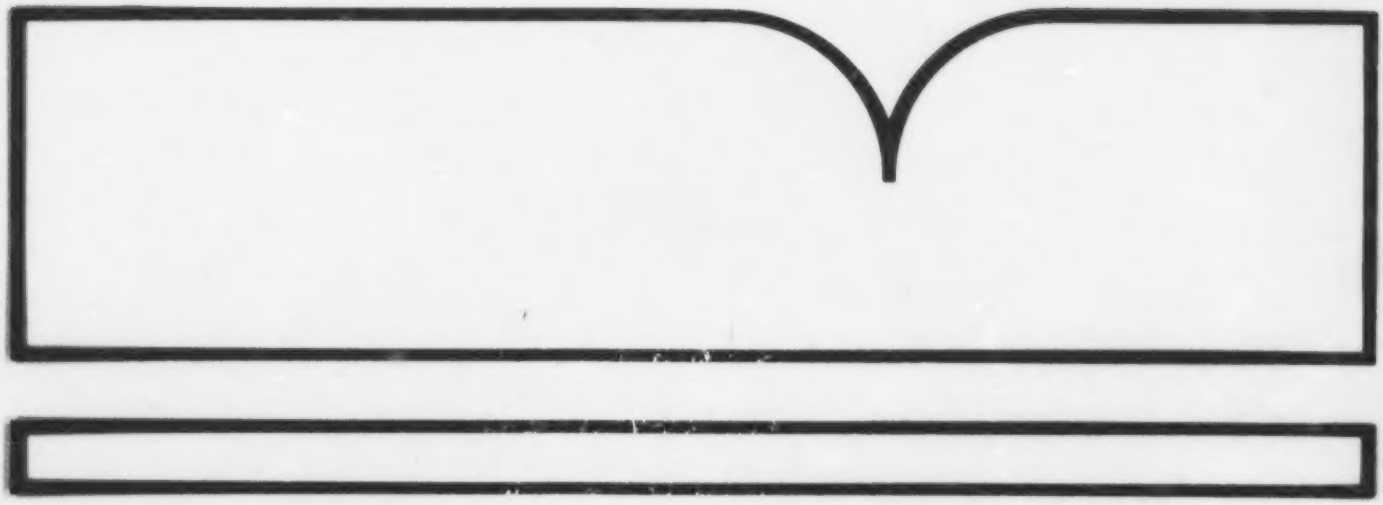

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16. ABSTRACT

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Transformation Pathways of Hexachlorocyclopentadiene in the Aquatic Environment

N. L. Wolfe, R. G. Zepp, P. Schlotzhauer and M. Sink

Environmental Research Laboratory
U.S. Environmental Protection Agency
College Station Road
Athens, Georgia 30613

ABSTRACT -- An environmental assessment of the transformation and transport pathways of hexachlorocyclopentadiene (hex) in simulated aquatic ecosystems is presented. Hydrolytic and photolytic disappearance rate constants in distilled and natural waters and in sediment-water systems are given. Sediments in defined sediment-water systems do not significantly affect the disappearance rate constants, compared to distilled water values, for the hydrolytic and photolytic processes. Water solubility, octanol/water partition coefficient, and vapor pressure for hex are also reported and compared with literature values. Fate and transport assessment using an evaluative model indicates that hex will not likely reach substantial steady-state concentrations in the various compartments of the simulated ecosystems. The results also indicate that photolysis and, to a lesser extent, hydrolysis are the predominant degradation processes; export via the water column is the predominant transport process.

INTRODUCTION

The chemical reactivity of hexachlorocyclopentadiene (hex) is reflected by its extensive use as an intermediate in the manufacture of other chemicals. Large scale production of this chlorinated hydrocarbon is prompted because it is an intermediate in the manufacture of insecticides, fire resistant resins and flame retardants (1,2).

Although hex is not applied directly to aquatic ecosystems, it can enter the aquatic environment through wastewater effluents in manufacturing processes or through spills such as occurred in Louisville in 1978 (1). Even though hex undergoes a variety of chemical reactions including addition, condensation, and substitution reactions (3), extrapolation of the extent to which these reactions occur under physical and chemical conditions that are common to aquatic environments has not been addressed (4). Even more important, certain physical properties of hex, along with its photochemical and hydrolytic reactivities, are needed to forecast its fate and transport processes.

Because hex is quite reactive, attempts to evaluate its environmental impact should not only include the parent compound, but also its reaction products because they can potentially exist at higher steady state concentrations than hex in aquatic ecosystems. Therefore, this report addresses the chemical and photochemical reactions of hex in water with emphasis on the kinetics of the reactions. The octanol-water partition coefficient, aqueous solubility, and Henry's Law constant of hex are reported. These data are then used in an evaluative model (5) to forecast exposure concentrations under physical and chemical conditions representative of selected aquatic environments common to the Southeastern United States.

MATERIALS AND METHODS

Materials

Hexachlorocyclopentadiene was obtained commercially (Aldrich Chemical Co.) and used as received. GC-MS analysis (see below) confirmed literature reports (1) that it contained small amounts of chlorinated hydrocarbons as impurities. (Tetrachlorobutadiene, 1.1% based on total ion current response, was found to be the major impurity.)

Analytical Procedures

Chemical analysis of hex was carried out using either liquid chromatography (LC) or gas-liquid chromatography (GLC). LC analysis was performed by making direct aqueous injections (50 µl) into a Micromeretics 7000 LC equipped with a variable wavelength detector usually set at 220 nm using a 50 cm x 2.2 mm i.d. ODS-2 column with the mobile phase 90% acetonitrile-water at a flow rate of 1.5 ml/min with a column pressure of 1350 psi. Analysis was performed also by first extracting hex from water using isooctane then analyzing the isooctane by GLC on a Tracor 222 Gas Chromatograph fitted with a ^{63}Ni electron capture detector and a 1.2 m x 0.64 cm i.d. column packed with 3% SE-30 on Chromosorb W. Injection port, column, and detector temperatures were 180, 125, and 250°C, respectively, with a flow rate of 60 cm^3/min. Product confirmation was carried out on a Finnigan Model 4021 Automated GS/MS/DS system equipped with EI.

Water Solubility Measurements

Water solubility measurements of hex were carried out using two different experimental techniques. The first involved equilibration of hex with distilled water through the vapor phase with an apparatus that has been described elsewhere (6). Hex was placed in a cup over a given quantity of water in a closed system and gently shaken. Water samples for analysis of hex were removed through a side arm that extended beneath the water layer and extracted directly into isooctane. The concentration of hex in the water was monitored until equilibrium was reached, usually between 5 and 10 hours.

The second method involved the addition of an excess of hex to distilled water with rapid stirring. Aliquots were withdrawn and centrifuged at 15,000 rpm for 15 min; an aliquot of the supernatant was extracted into isooctane and analyzed to determine the concentration of hex.

Octanol-Water Partition Coefficient

Three 10-mg samples of hex were dissolved in 2 ml of 1-octanol and equilibrated with 40 ml of water (octanol saturated) and shaken for 15 min. One ml of the aqueous layer was extracted with 10 ml of isooctane and analyzed by GLC. One-half ml of the octanol layer was diluted to 10 ml in hexane and analyzed by GLC. The octanol-water partition coefficient was calculated as described elsewhere (7).

Vapor Pressure

Three 100-mg samples of hex were placed in Mininert test tubes fitted with teflon septums and allowed to equilibrate. The head space was sampled (50 µl) with a gas-tight syringe containing 10 µl of isooctane. The contents of the syringe were injected into 10 ml of isooctane followed by rinsing. The vapor pressure of hex was then calculated based on the concentration of hex determined in the organic layer.

Henry's Law Constant

In a similar set of experiments, three 5-ml samples of an aqueous solution of hex were allowed to equilibrate with the head space in Mininert tubes. The head space was sampled as described above and the concentration of hex determined. Inversion of the tube, with time allowed for equilibration, permitted the sampling of the aqueous phase. Thus, experimental values of the gas and aqueous phase equilibrium concentrations permit the calculation of Henry's Law constant (8).

Hydrolysis

A typical hydrolysis procedure is described as follows (9). A 40-ml sample of a water saturated solution, prepared by volatilization of hex into water, was diluted to 50 ml with 5 ml of $NaHCO_3$ (5×10^{-2} M) and 5 ml of Na_2CO_3 (5×10^{-2} M). The hydrogen ion activity of the resulting solution was determined with a pH meter calibrated with standard buffers chosen to encompass the calculated pH. Aliquots were then pipetted into 5-ml ampoules (or Mininert tubes) filled to near capacity to minimize the head space. The ampoules were then placed in a constant temperature bath at 30° ± 0.2°C, allowed to thermally equilibrate and then removed at predetermined time intervals. The ampoules were opened, aliquots withdrawn and the hydrolysis reaction quenched by addition of an aliquot to 5 ml of isooctane using a gas tight syringe for the transfer. The reaction mixture was monitored for hex through approximately two halflives. An ampoule was saved for analysis at the end of a calculated 10

half-life interval. A similar procedure was employed in which 50-µl aliquots were withdrawn from a 50-ml reaction flask and analyzed directly by LC.

Rate constants were obtained by linear least squares analysis of the concentration-time data using the integrated form of the first-order rate equation,

$$\ln \frac{C_o - C_\infty}{C_t - C_\infty} = kt \qquad (1)$$

where C_o, C_∞, and C_t are the concentrations of hex at time zero, after 10 half lives, and the given time interval, respectively.

Sediment Mediated Hydrolysis

Ten 100-mg samples of processed and characterized sediments (10) were placed in 25-ml erlenmeyer flasks fitted with ground glass stoppers. The samples were heat sterilized, allowed to stand 24 hours and resterilized. Sterile water (20 ml) was added to each flask and then the sediment-water contents were spiked with 10 µl of hex (1×10^{-4} M) in acetonitrile. Flasks were then placed in a rotatory shaker thermostated at 30 + 1°C. Flasks were removed at given time intervals, and the entire contents were extracted by adding 1 ml of acetonitrile followed by 4 ml of isooctane. The flasks were vortex mixed for 1 minute followed by sonification for 1 hour. The organic layer was analyzed for hex by GLC. Sterility checks (plate counts) were made at time zero and at the end of approximately two half-lives. A sample was saved for analysis at the end of a calculated 10 half-lives interval. The rate constants were determined as described above.

Because of the large Henry's Law constant for hex, volatilization into the head space of reaction vessels is a potential problem in water and sediment-water studies. To account for this in the most general case, sediment-water-air partitioning, the following representation is convenient

$$Hex_{(S)} \overset{K_p}{\rightleftharpoons} Hex_{(W)} \overset{H}{\rightleftharpoons} Hex_{(A)} \qquad (2)$$

where the subscripts S, W, and A are the sediment, water, and air concentrations of hex, respectively; K_p and H are the sediment-water partition coefficient and Henry's Law constant, respectively. It is then readily shown that, at equilibrium, the fraction of the compound in the vapor phase is given by

$$\frac{Hex_{(A)}}{Hex_{(T)}} = \frac{\rho' H/RT}{1 + \rho K_p + \rho' H/RT} \qquad (3)$$

where $Hex_{(T)}$ is the total amount of hex in the system, R is the gas constant, and T is the temperature (°K); and ρ and ρ' are sediment to water and air to water ratios, respectively.

Thus in the case of a given sediment-water study, the fraction of hex present in the head space is readily calculated. For example, using 0.4 g of sediment in 20 ml of water in a 25-ml flask gives approximately 5 ml of head space in the reaction vessel. Using the calculated K_p value of 1300 and H of 27 atm m^3/mole (8), the fraction of hex in the head space is 0.008. In most kinetic studies, the fraction of hex in the head space was calculated to be less than 2 percent, and in view of other experimental variations, the rate constants were not corrected for this phenomenon.

Photochemical Kinetics Studies

To obtain a preliminary idea of the photoreactivity of hex, aqueous solutions containing hex at concentrations below its solubility limit were exposed to sunlight at Athens, GA, during November and December 1980. The solutions were exposed in a series of 13 mm i.d. borosilicate test tubes that were completely filled and that were equipped with gas-tight Mininert teflon-lined valves. Hex was introduced into the water by placing the tubes, filled with equal volumes of water, in a closed container with a small beaker containing a few drops of hex. The hex volatilized into the water yielding approximately equal concentrations in each tube. The tubes were exposed to sunlight positioned with a slight downward tilt over grass in an open field. The solutions, after exposure to sunlight for varying time intervals, were analyzed directly by HPLC. The concentration of hex in each tube was analyzed before and after

irradiation. Hex was so reactive that the solar irradiance remained almost constant during the first two half-lives in sunlight (15 minutes or less). Experiments were on both clear and overcast days and in distilled water or a natural water sample collected from the top meter of the Aucilla River, a black water system near Lamont, FL. Experiments with suspensions of well-characterized sediments or a turbid water sample from the Oconee River, Athens, GA, were conducted in a similar fashion, although solutions were analyzed by GLC as described above. Photolysis rate constants were computed using the integrated first order rate equation.

The electronic absorption spectrum of hex was obtained in a mixture of 50% acetonitrile and water. The reaction quantum yield at 313 nm was determined in a merry-go-round photochemical apparatus (11) employing a procedure that is discussed elsewhere (12). A benzophenone-cis-1,3-pentadiene actinometer (13) was used to determine the light intensity.

EVALUATIVE MODEL

Simulation studies of the behavior of hex in synthesized aquatic environments were carried out using the Exposure Analysis Modeling System (EXAMS) (14). EXAMS is a multicomponent kinetics model that utilizes fate and transport processes to assess exposure concentration and to evaluate the contribution of the various processes in selected aquatic environments.

Four EXAMS environments were simulated: a small eutrophic pond with a 31-day retention time in the water column; an oligotrophic stratified lake and a eutrophic stratified lake each with an area of about 35 ha; and a 35-km long river segment, 100 m wide with a detention time of 1 hour. For more details on the physical, chemical, and biological characteristics of the ecosystems used in EXAMS, the reader should consult reference 14.

DISCUSSION

Degradation Pathways

Hydrolysis. The hydrolysis studies (Table 1) show that the reaction rate constant over most environmental pH's is independent of pH and can be adequately described by a neutral hydrolysis rate constant k_{H_2O}. The average value and standard deviation of all the runs over the pH range of about 3 to 10 is $(1.5 \pm 0.6) \times 10^{-6} sec^{-1}$ at 30°C. The activation parameters are calculated from the average value of the data sets at 30, 40, and 50°C. Ea, the activation energy, and A, the Arrhenius constant, were obtained by a linear regression

Table 1. First-order Hydrolysis Rate Constants for Hex in Water[a]

pH	k, $sec^{-1} \times 10^5$	Temperature °C	Buffer
2.88	1.16	30	HCl
	0.93	30	HCl
5.08	1.44	30	AcONa/AcOH
	1.11	30	AcONa/AcOH
6.70	2.59	30	NaH_2PO_4/Na_2HPO_4
	2.26	30	NaH_2PO_4/Na_2HPO_4
9.76	1.16	30	$NaHCO_3/Na_2CO_3$
	1.40	30	$NaHCO_3/Na_2CO_3$
7.0	4.4	40	--
	5.0	40	--
7.0	12.0	50	--
	13.0	50	--

[a]Activation parameters were calculated from average value of rate constants obtained at 30, 40 and 50°C. Ea = 20.8 ± 1.6 cal/mole, ln A = 21.5 ± 2.7.

analysis of the data from the Arrhenius equation $k = A\, e^{-Ea/RT}$ and are given in Table 1. It is evident from Table 1 that no major buffer catalyst affects the rate constants. It was also found that the addition of NaCl to give a 0.5 M solution did not affect the hydrolysis rate constants significantly. This suggests that these rate constants would be applicable to marine environments as well.

Hydrolysis studies in several sediment suspensions revealed that the hex hydrolysis rate constant was unaffected by the addition of various amounts of sediments to the aqueous solutions of hex. Using processed sediment samples, both sterilized and unsterilized, and estimating the fraction sorbed indicated that as the fraction of hex sorbed varied from 0 (no sediment) to greater than 0.92, the rate constant varied less than a factor of 2 (Table 2). Thus if the sediment were actually protecting hex from the neutral hydrolysis reaction in the aqueous phase, the observed rate constant would have been expected to be retarded by a factor of at least 50. In the evaluative model, therefore, the rate constant for hex in the sediment was assumed to be the same as that in water.

Photolysis. Kinetic studies of the photolysis of hex were conducted to provide a basis for quantitative estimation of its photolysis rates in various aquatic environments. All photolysis experiments were carried out in sufficiently short time intervals that hydrolysis of hex was a negligible competing process, as shown by dark controls.

Preliminary studies were conducted with sunlight as the light source. The studies involved photolysis of hex dissolved in distilled water and in several natural water samples at depths of 1 to 4 cm. The natural waters used in these studies were selected because they contained high concentrations of either humic substances (Aucilla River) or suspended sediments (obtained from various rivers in the United States). Photolysis in natural waters can potentially be initiated by direct absorption of sunlight by the pollutant as well as by other competing pathways that involve dissolved and suspended matter. In distilled water, direct photolysis is the only mechanism for photoreaction. By comparing photolysis rate constants of hex in distilled and natural waters exposed at the same time to sunlight at shallow depths, it was possible to determine the extent to which the dissolved humic substances or sediments influenced the photolysis. Recent studies by Zepp et al. (15) and Mill et al. (16) have shown that photosensitized or free radical oxidations occur most rapidly in natural waters, such as

Table 2. Decay Rate Constants for Hex in Sediment-Water Systems

Sample	Sediment Concentration g/100 ml	Decay Rate Constant k, sec^{-1}, x 10^5	Fraction in Solution x/T[a]
EPA-13[b]	0.0	1.5 ± 0.6[d]	1
	0.05	3.5 ± 0.4	0.79
	0.10	4.4 ± 0.3	0.65
	0.15	4.5 ± 0.5	0.55
	0.20	3.7 ± 0.4	0.48
	0.40	2.7 ± 0.3	0.32
	1.0	3.4 ± 0.3	0.16
	2.0	2.1 ± 0.4	0.08
Oconee River (GA)	1.0[c]	1.78 ± 0.09	
	1.0	1.5 ± 0.2	
USDA (pond, GA)	1.0[c]	1.8 ± 0.3	
	1.0	2.0 ± 0.2	
Hickory Hills (pond, GA)	1.0[c]	3.4 ± 0.7	
	1.0	5.4 ± 0.7	

[a]The fraction of hex in solution (x/T) was calculated using a value of K_p obtained by the relationship between K_{OC} and K_{OW} as described by Hassett et al. (10). [b]Organic content of the sediment is 3.0 . [c]Sterile systems. [d]Average value from Table 1.

the Aucilla River, that contain high concentrations of humic substances. Our studies, however, indicated that the photolysis of hex in sunlight was actually slightly slower in Aucilla River water than in distilled water (Figure 1). The slowdown could be accounted for by light attenuation effects upon direct photolysis. Likewise, as in the case of hydrolysis, the presence of suspended sediments had little effect upon the photolysis rate of hex as compared to distilled water (Table 3). These results indicate that direct photolysis of hex in natural waters is so rapid that other light-induced processes cannot successfully compete with it. In all cases, photolysis half-lives in midday sunlight (Athens, GA, latitude 34°N, 83°W) were found to be less than 10 minutes.

The direct photoreaction of hex in water was also studied under controlled conditions in the laboratory. The reaction quantum efficiency ϕ_r was determined to be 0.26 employing monochromatic light (313 nm) isolated by filters from a mercury lamp. The electronic absorption spectrum of hex (Figure 2) was used in conjunction with the reaction quantum yield and the simulated solar spectral irradiance (17) to compute photolysis rate constants for hex as a function of location and time. Rate constants computed for Athens, GA, were in close agreement with those observed in the sunlight experiments described above. For use in the EXAMS model, rate constants were computed for various times at latitude 40°N, the latitude that approximately bisects the United States. At this latitude, the near-surface photolysis rate constant of hex on cloudless days averaged over both light and dark periods for a year was computed to be 3.9 hr^{-1}.

All computations in the EXAMS model are corrected for the influence of light attenuation and clouds (18-20). In a water column of depth Z, equation (4) was employed to calculate the effects of light attenuation on photolysis.

$$k_p(z) = k_p(0) \frac{1-e^{-Kz}}{Kz} \qquad (4)$$

where $k_p(z)$ is the average photolysis rate constant in a water column of depth z,
$k_p(0)$ is the near-surface photolysis rate constant, and
K is the mean diffuse attenuation coefficient of the water body (18).

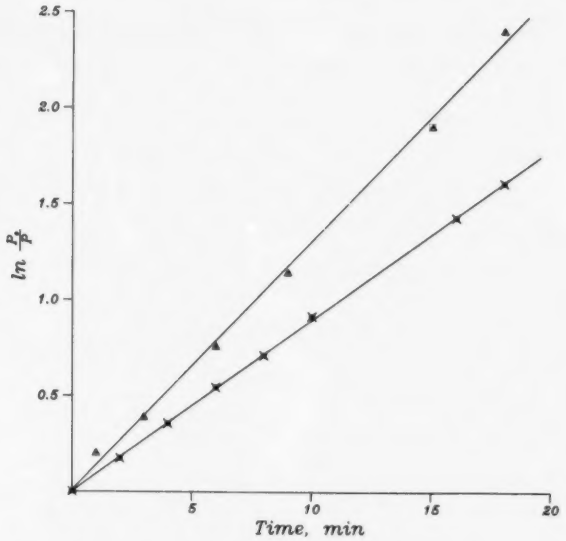

Figure 1. Kinetic data for photolysis of hexachlorocyclopentadiene (1.8×10^{-7} M) in distilled water (Δ) and in Aucilla River water (o) where P_0 is initial concentration of hex and P is its concentration after exposure for various times to sunlight on an overcast day during November 1980 at Athens, GA.

Table 3. Effects of Suspended Sediments on the Sunlight Photolysis Rates of Hexachlorocyclopentadiene (1.5×10^{-7} M)

Source of Sediment	Sediment Concentration, mg/l	Sunlight [a] $k_p hr^{-1}$	Ratio [b]
North Oconee River, Athens, GA	0	19.9 ± 0.7	
	45	19.7 ± 1.5	0.99 ± 0.11
	0	10.9 ± 0.8	
	45	9.5 ± 0.6	0.87 ± 0.12
Mississippi River, McClure, IL	0	19.9 ± 0.7	
	59	18.7 ± 0.7	0.94 ± 0.06
	0	10.9 ± 0.8	
	59	9.9 ± 0.4	0.91 ± 0.10
Ohio River, Ceredo, WV	0	19.9 ± 0.7	
	63	16.8 ± 2.2	0.84 ± 0.14
Missouri River, Stanton, ND	0	3.8 ± 0.5	
	61	5.3 ± 0.3	1.4 ± 0.26
	0	4.4 ± 0.4	
	61	5.1 ± 0.2	1.2 ± 0.17
Ohio River, Ripley, OH	0	3.8 ± 0.5	
	63	5.2 ± 0.3	1.4 ± 0.26
	0	4.4 ± 0.4	
	63	4.9 ± 0.2	1.1 ± 0.16

[a]Exposed to sunlight in 13 mm o.d. test tubes (1 cm light pathlength); each rate constant average of three points. [b]Ratio of rate constant in suspension to rate constant in distilled water.

Reasonable values for K were estimated from measurements by Calkins of the penetration of solar ultraviolet light into various natural waters (19). Calkins employed a Robertson-Berger meter for these measurements and the response curve for this meter is very similar to the absorption spectrum of hex. The photolysis rate constants are also corrected for the average influence of clouds as described by Mo and Green (20) employing eq. 5 where F is the ratio of the light intensity in the presence and absence of clouds and C is the cloud cover in tenths.

$$F = 1 - 0.056C \qquad (5)$$

Values of K used in the model discussed below were: river, 3.0 m^{-1}; pond 2.0 m^{-1}; eutrophic lake 2.0 m^{-1} (littoral zone, epilimnion), 1.0 m^{-1} (hypolimnion); oligotrophic lake, 2.0 m^{-1} (littoral zone), 0.19 m^{-1} (epilimnion), 0.1 M^{-1} (hypolimnion). Cloud covers assumed (in tenths) were river, 3; pond, 4; eutrophic lake, 5; oligotrophic lake, 5.

Physical Constants

Octanol-Water Partition Coefficient and Water Solubility. The octanol-water partition coefficient (K_{ow}) for hex was measured to be $(1.1 \pm 0.1) \times 10^5$ at 28°C (7). This value compares to that of 1×10^5 obtained by McDuffie using LC to estimate octanol/water partition coefficients (21). The experimental value was used to calculate the sediment organic carbon-water partition coefficient (K_{OC}) of 12,000 from the relationship of Hassett et al. (10). The water solubility (K_S) was measured to be 1.8 ± 0.6 mg/l at 28°C, where this value represents the average of the two methods described above. This value is near that of 0.8 mg/l reported by Lu et al. (4) at 25°C.

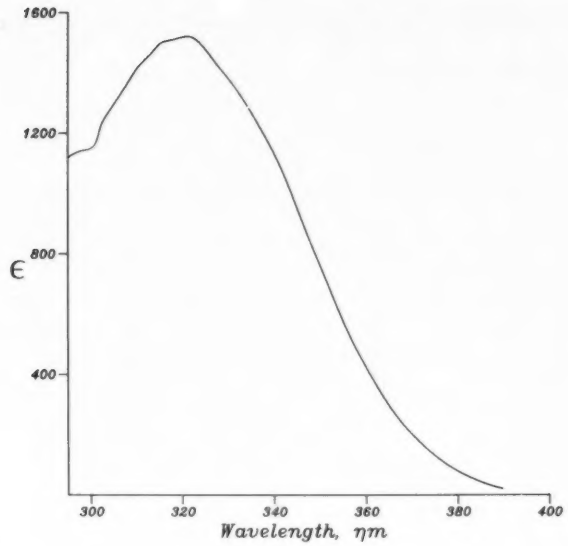

Figure 2. Electronic absorption spectrum of hexachlorocyclopentadiene in 50% acetonitrile-water. The symbol ε is the molar absorptivity.

Henry's Law Constant. The Henry's Law constant was measured directly by analysis of a solution at equilibrium of hex in water in a closed container. The value was determined to be 0.027 + 0.010 atm m^3/mole (8). This value corresponds with that of 0.016 atm m^3/mole calculated from the measured vapor pressure (0.08 mm Hg at 25°) and the measured water solubility.

Environmental Fate and Transport Assessment of Hex

To assess the behavior of hex in the aquatic environment, the EXAMS model was used. This model has been described in detail elsewhere and only the results are presented. Table 4 contains the chemical and physical constants used in the model. Table 5 contains the output for the four ecosystems that were described earlier.

Table 4. Summary of Constants Used in EXAMS at 25°C in Water.

K_S, mg/l	1.8
K_H, atm m^3/mole	2.7×10^{-2}
K_{OW}	1.1×10^{5}
K_P, hr^{-1}	3.9
$k_{H\ O}$, hr^{-1}	4.0×10^{-3}[a]
K_{OX}, $M^{-1}sec^{-1}$	1×10^{-10}[b]
k_B, ml $org^{-1}hr^{-1}$	1×10^{-5}[c]

[a]Extrapolated to 25°C using the data in Table 1. [b]Estimated using data in Reference 27. [c]This is a maximum value based on the observation that there was no detectable difference in the hydrolysis rate in either sterile or non-sterile studies and measured organism numbers.

Table 5. Summary of Results of Computer Simulation of the Fate and Transport of Hexachlorocyclopentadiene in Four Typical Aquatic Environments.

	River	Pond	Eutrophic Lake	Oligotrophic Lake
Distribution ( )				
Water Column	1.22	14	12.97	32.91
Sediment	98.78	86	87.03	97.09
Recovery Time[a], days	52	81	58	87
Load Reduction ( ) by Processes				
Hydrolysis	8.04	17.85	8.29	16.50
Oxidation	0.00	0.00	0.00	0.00
Photolysis	18.68	80.39	89.18	82.41
Biolysis	0.57	0.23	0.30	0.01
Volatilization	0.69	1.33	1.56	1.08
Export[b]	72.02	0.20	0.01	0.00

[a] The time required to reduce the steady-state concentration by five half-lives.
[b] Physical loss from the system by any pathway other than volatilization.

In the river simulation, export from the ecosystem, along with photolysis, are the dominant processes with hydrolysis and biolysis being too slow to compete. In the pond, eutrophic lake, and oligotrophic lake environments, photolysis is the dominant process accounting for more than 80 of the transformation in all three ecosystems. Volatilization appears as a competing process and contributes a small amount to the overall reduction as does hydrolysis.

Even though hex is quite reactive, the recovery times in the pond and lakes are on the order of 3 to 4 months. This is because of the slow release of hex from the bottom sediments where the photolytic process is retarded.

Products

Hydrolysis. Because hex is quite reactive in the above pond and lake environments, both hydrolytically and photochemically, a preliminary investigation was carried out to determine the products. Previous studies under somewhat different reaction conditions by other investigators indicated that hex products may arise via a reactive intermediate and several different products have been reported depending on the reaction conditions (22,23,24,25). Unfortunately, no product peaks were observed during the course of the kinetic studies in which hex concentration was monitored by either GLC or LC analysis. Also, in a separate study at 50°C for 10 days in 95 ethanol no detectable reaction had occurred, based on the initial concentration, as shown by GLC analysis.

A preparative hydrolysis reaction at 60-70°C in 40 acetonitrile-water at 10^{-4}M hex was carried out. The reaction proceeded through approximately two half-lives. Then exhaustive extraction with benzene followed by concentration of the isooctane layer and subsequent analysis of the organic layer by GC-MS showed nine major peaks in the chromatogram. Based on the mass spectra, several of these peaks were high molecular weight compounds but identification was not positive. In the case of the lower molecular weight products, it could not be determined whether they were isolatable intermediates or arose from thermolyis of higher molecular weight compounds in the injection port. If in fact these products are formed in solution, then they are suggestive of the formation of an unstable, reactive intermediate that reacts further, either with itself or other species in solution, to give a variety of isolatable products. It is also anticipated that the products formed would be a function of the initial concentration of hex and the concentraton of other species in solution.

Photolysis. Products formed from the photolysis of hex in dilute aqueous solution were also elusive. Studies in methanol at high concentrations of hex gave a product that had a retention time and a mass spectrum identical to that of the dimethyl ketal of tetrachlorocyclopentadienone (an authentic sample was synthesized by the previously described procedure) (26). In water, several chlorinated photoproducts with higher molecular weights than hex were detected using GC-MS analysis of the reaction mixture. These experiments suggest that photolysis, like hydrolysis, also yields a reactive intermediate.

CONCLUSION

Results of model simulation of the fate and transport of hexachlorocyclopentadiene (hex) in various simulated ecosystem environments suggest that hex is transformed predominantly via photolysis and to a lesser extent hydrolysis. These results also suggest that in river systems export from the ecosystem will be the dominate pathway, but in the lake and pond environments transformation will dominate.

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